Materials Research Bulletin 90 (2017) 87–93

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Preparation of In_2O_3 crystals in phase separated structure of sodium borosilicate glass and its electrical conductivity

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ARTICLE INFO

Article history:
Received 6 October 2016
Accepted 12 February 2017
Available online 20 February 2017

Keywords:
A. Glasses
B. Crystal growth
C. X-ray diffraction
D. Electrical properties

ABSTRACT

The preparation of In_2O_3 crystals in phase separated structure of sodium borosilicate (Na_2O-B_2O_3-SiO_2) glass was successfully obtained by melt quenching method and its electrical conductivity was successfully clarified.

Sodium borosilicate glass is phase separated into silica (SiO_2) phase and sodium borate phase (Na_2O-B_2O_3). The sodium borate phase mainly contains ionic bondings, and the generation and growth of crystals can easily occur in this phase for its high solubility of various kinds of ions. In this study, a glass ceramics was prepared by precipitating In_2O_3 crystals in the sodium borate phase of the sodium borosilicate glass. After acid leaching of the sodium borate phase, the In_2O_3 X-ray diffraction peaks that were observed after crystallization treatment disappeared, indicating that In_2O_3 crystals were selectively precipitated in the sodium borate phase. By decreasing the proportion of the sodium borate phase which was achieved via controlling the amount of B_2O_3 in the glass, In_2O_3 crystals precipitated continuously in this phase, resulting in an increase in the electrical conductivity from 3.30×10^{-5} S/cm to 6.56×10^{-5} S/cm at 500 °C and a decrease in the activation energy from 36.6 kJ/mol to 27.0 kJ/mol, respectively. Furthermore, the electrical conductivity increased by Sn doping and introduction of oxygen vacancies via H_2 reduction into the In_2O_3 crystal lattice.

1. Introduction

Recently, a new approach to prepare novel glass materials with excellent shapability and high functionalities by controlling their fine structure has become very important [1–4]. More specially, phase separation and crystallization are considered to be key processes in the preparation of these fine structured materials [5–12].

Sodium borosilicate glass (Na_2O-B_2O_3-SiO_2) exhibits phase separation into two phases: the SiO_2 phase and the Na_2O-B_2O_3 (sodium borate) phase as shown in Fig. 1 [13]. Since the sodium borate phase is mainly ionic in nature, the generation and growth of crystals easily occur in this phase due to its high solubility of various kinds of ions [14]. Further, the size of the crystal and its connectivity in this phase can be controlled by tailoring the phase separated structure (Fig. 1). Using this concept, the authors have published the papers about highly photocatalytic and highly photo luminescent glass ceramics with TiO_2 [15] and YBO_3:Eu^{3+} crystals [16], respectively.

In_2O_3 is well known as a transparent electrically conducting crystal [17]. In_2O_3 emits an electron or a hole upon doping with different kinds of atoms or introduction of oxygen vacancy in the crystal lattice [18,19]. As shown in Fig. 1, the connectivity and density of the crystals precipitated in the sodium borate phase are expected to increase. Based on this preparation process, the porocification of these glasses is easily achieved [15]. One of the most fascinating targets of this transparent porous glass ceramics with electron conductivity is in its use as electrode for the light reaction in the field of artificial photosynthesis [20].

In this paper, the preparation of a glass ceramics with In_2O_3 crystals precipitated into the sodium borate phase and its electrical conductivity are described. The effects of introducing Sn into the In_2O_3 crystal lattice as well as H_2 reduction are also discussed.

2. Experimental

2.1. Preparation of glass samples

The glass sample was prepared by melting the mixture of the analytical grade reagents of In_2O_3, SiO_2, $B(OH)_3$, Na_2CO_3, and SnO_2 at 1350 °C and 1500 °C for 2 h in an alumina crucible followed by

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http://dx.doi.org/10.1016/j.materresbull.2017.02.020
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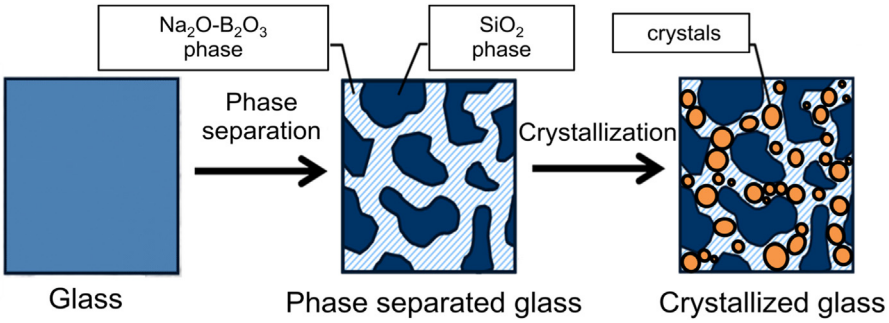

Fig. 1. Schematic illustration of phase separation and crystallization in the borosilicate glass.

rapid quenching using a stainless steel press. The composition employed here was $8.7In_2O_3 – 56.5SiO_2 – 13.1B_2O_3 – 21.7Na_2O$ (mol %). As shown in Table 1, the amounts of SiO_2 and B_2O_3 were varied to control the composition of the phase separated structure. A Sn doped sample was prepared with keeping Sn/In = 0.05 was also prepared.

2.2. Phase separation and crystallization

The obtained glass was heat treated at 800 °C for 15 h for phase separation and crystallization. To detect the phase separated structure, the glass samples were leached with an aqueous solution of 3N HNO_3 at 60 °C for 24 h. Since the acid leaching creates pores that are also present in the phase separated structure, the microstructure of the sample after leaching was observed using field emission scanning electron microscope (FE-SEM, JSM-7001F, JAPAN ELECTRON OPTICS LABORATORY Co.) and the specific surface area was measured. The surface area was calculated from N_2 adsorption isotherm measured at 77 K using BET method (BELSORP-mini, BELL JAPAN INC.).

The crystals precipitated in the glass were detected by X-ray diffraction (XRD, UltimaIV, Rigaku Co.). CuKα irradiation at 40 kV and 40 mA was used as the X-ray source for the measurement and diffractograms were recorded by step scanning in the 2θ range of 10°–80° with a step interval of 0.02. From the diffraction profile obtained by XRD measurement, the identification of crystalline in the glass was performed by X-ray analysis software, Jade7 (v.7.5.13. Materials Date Inc.).

2.3. Measurement of electrical conductivity

The electron conductivity was measured by galvanostat (HA-151B, HOKUTO DENKO Co.). Direct current (DC) conductivity measurements were performed at temperatures ranging from 100 °C to 500 °C under Ar atmosphere. The surfaces of the samples were polished with SiC waterproof abrasive paper prior to electrical conductivity measurements. Silver paste (RD-550, Fujikura Kasei Co.), applied on both sides of the samples, served as the electrode. Electrical conductivity was also measured for the sample heat treated under H_2 atmosphere at 750 °C for 1 h.

Table 1
Glass compositions changing SiO_2 and B_2O_3 amount.

	In_2O_3	SiO_2	B_2O_3	Na_2O
$B_2O_3 = 11$	8.7	58.6	11.0	21.7
$B_2O_3 = 13$	8.7	56.6	13.0	21.7
$B_2O_3 = 16$	8.7	53.6	16.0	21.7
				(mol%)

3. Results and discussions

3.1. Phase separation and crystallization

3.1.1. Glass melting temperature

Figs. 2 and 3 show the X-ray diffraction (XRD) patterns of glass samples melting at 1350 °C and 1500 °C, before and after crystallization treatment, respectively. The marks ■ and ● in the figure are used to denote $InBO_3$ and In_2O_3 peaks, respectively. The data in the figure indicate that insulating $InBO_3$ crystal is the main crystalline phase in the glass melting at 1350 °C whereas, electrically conductive In_2O_3 crystal is the main crystalline phase in the glass melting at 1500 °C. This may be caused by the large amount of Al_2O_3 eluted from the alumina crucible into the sample at 1500 °C. From EDS (Energy Dispersive X-ray Spectrometry) analysis (FE-SEM, JSM-7001F, JAPAN ELECTRON OPTICS LABORATORY Co.), the compositions of the glasses melting at 1350 °C and at 1500 °C were determined to be $8.5In_2O_3 – 55.0SiO_2 – 12.8B_2O_3 – 21.1Na_2O – 2.6Al_2O_3$ (mol%), and $7.9In_2O_3 – 51.6SiO_2 – 12.0B_2O_3 – 19.8Na_2O – 9.5Al_2O_3$ (mol%), respectively. The presence of Al_2O_3 constituent in sodium borosilicate glass suppresses its tendency of phase separation [21]. At 1350 °C, due to the lilatively lower temperature, the amount of Al_2O_3 eluted from the alumina crucible is small. Consequently, since the tendency of phase separation is large and the B content in the sodium borate phase is high, $InBO_3$ crystals grow predominantly in the sodium borate phase [16]. On the contrary, at 1500 °C, as the amount of eluted Al_2O_3 constituent from the alumina crucible is higher, the tendency of phase

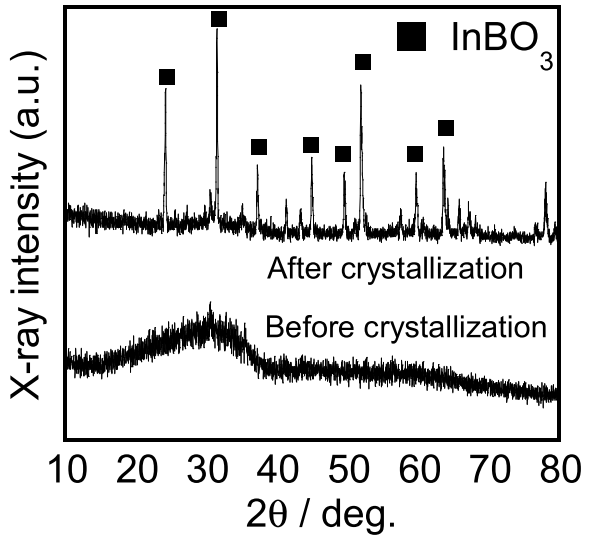

Fig. 2. XRD patterns of before and after crystallization treatment in the glass samples melting at 1350 °C, without Al_2O_3 addition.